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SUPERCRITICAL FLUID EXTRACTION OF POLYCHLORINATED DIBENZO-p-DIOXINS FROM MUNICIPAL INCINERATOR FLY ASH

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MANAGEMENT PERSPECTIVE

This report describes the results of a study on the optimization of statistically important parameters associated with the extraction of polychlorinated dibenzo-p-dioxins from municipal incinerator fly ash samples.

The study has shown that quantitative recovery of the compounds of interest can be achieved using the supercritical fluid extraction protocol outlined in the report. By shortening the time required for the extraction step, the methodology contributes to reducing the entire analysis time to ca 2 hours per sample, a significant improvement over the ca. 24 hours/sample required with conventional extraction procedures. The new methodology has advantages over organic solvent-based extraction techniques in terms of occupational health and safety. For the moment, these time saving and safety benefits are partially offset by the high cost of the equipment needed to carry out supercritical fluid extraction.

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PERSPECTIVE GESTION

Dans ce rapport on donne les résultats d'une étude portant sur l'optimisation de paramètres d'importance statistique associés à l'extraction des dibenzo-p-dioxines polychlorées des échantillons de cendres volantes provenant des incinérateurs municipaux.

L'étude a montré qu'il est possible de récupérer quantitativement les composés en question par la méthode d'extraction au fluide supercritique décrite ici. Comme l'extraction proprement dite est plus rapide, la méthode permet de réduire le temps d'analyse à environ 2 heures par échantillon, une amélioration notable si l'on compare aux quelque 24 heures par échantillon des méthodes avec extraction classique. Au point de vue de la santé et de la sécurité, cette nouvelle méthode est préférable aux techniques d'extraction aux solvants organiques. Pour le moment, les avantages qu'elle présente en raison de sa rapidité et de sa sûreté sont en partie réduits du fait que l'équipement nécessaire pour l'extraction au fluide supercritique est très coûteux.

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ABSTRACT

Supercritical fluid extraction can be used to extract chlorinated dibenzo-p-dioxins from fly ash. The ability of supercritical fluid extraction (SFE) to remove polychlorinated dibenzo-p-dioxins (PCDDs) from an incinerator fly ash sample was investigated employing supercritical nitrous oxide and its mixtures with methanol, and toluene. The use of a virtually inert fluid such as pure nitrous oxide provides significant improvement over conventional extraction procedures in that no solvent residue is left in the processed extract. Recoveries of individual PCDD congeners were calculated from the analysis of C-13 labelled dioxins employing selected ion monitoring high resolution gas chromatography-mass spectrometry (HRGC/MS).

The extraction procedure was compared to the Soxhlet extraction currently used as a standard method for removing chlorinated dibenzo-p-dioxins from fly ash samples. The results indicate that the time required for the extraction and cleanup can be shortened from 24 to 2.5 hours/sample. Quantitative recovery of chlorinated dibenzo-p-dioxins (PCDDs) at μg/kg level with a relative standard deviation ranging from 1.8 to 5.8 % was achieved.

RÉSUMÉ

L'extraction au fluide supercritique peut servir à extraire les dibenzo-p-dioxines chlorées des cendres volantes. On a évalué l'efficacité de cette méthode pour l'extraction des dibenzo-p-dioxines polychlorées (PCDD) des cendres volantes au moyen d'oxyde nitreux supercritique seul ou en mélange, soit avec du méthanol, soit avec du toluène. L'utilisation d'un fluide pratiquement inerte comme l'oxyde nitreux pur est une amélioration notable par rapport aux méthodes d'extraction classiques, car il ne reste aucun résidu de solvant dans l'extrait. On a évalué la récupération de certains congénères de PCDD d'après les résultats de l'analyse de dioxines marquées au C-13 par chromatographie en phase gazeuse à haute puissance résolution et spectrométrie de masse à détection ionique sélective (CGHP/SM).

On a fait une étude comparative entre la méthode d'extraction présentée et l'extraction au Soxhlet, actuellement la méthode standard pour l'extraction des dibenzo-p-dioxines chlorées des cendres volantes. D'après les résultats obtenus, le temps d'extraction et de nettoyage peut être réduit de 24 heures à 2,5 heures par échantillon. On a pu récupérer récupération quantitativement des dibenzo-p-dioxines chlorées (PCDD) à des concentrations de l'ordre du µg/kg avec un écart-type relatif de 1,8 à 5,8 %.

INTRODUCTION

Supercritical fluids are finding acceptance as solvation media in environmental analytical chemistry. Most reported applications of supercritical fluid extraction (SFE) deal with coupling of small volume extractors to high resolution gas chromatographs (HRGC). These two techniques in tandem or off-line, may speed-up the analyses of contaminants in various matrices. Perhaps the most difficult matrix is fly ash, formed during combustion of municipal garbage. Fly ash contains up to 99% of inorganic matter. The predominant elements in fly ash are carbon (up to 35%), silicon (7 to 20%), aluminum (3 to 12%), iron (1 to 7%), calcium (0.1 to 2%), and sulfur (0.1 to 1%) and many trace elements.

The analytical procedures and instrumentation used to determine polychlorinated dibenzo-p-dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs) in fly ash have been refined considerably (1,2). Because very low concentrations are being determined, sample extraction and clean-up requires time consuming multi-step separation procedures. The PCDDs and PCDFs are normally recovered from fly ash samples by solvent extraction in a Soxhlet apparatus, followed by cleanup and concentration steps. Although many procedures have been published, the most commonly used one requires acid treatment with 3 percent HCl followed by 20 hours Soxhlet extraction with toluene (3).

In 1989, we described a SFE technique as part of the determination of 2,3,7,8-TCDD in sediment samples (4). Nitrous oxide and nitrous oxide + methanol (2%) were used as the supercritical fluids, both under static and dynamic modes of operation. Recently Alexandru et al. (5) compared the results obtained for the extraction of PCDDs and PCDFs from fly ash samples when using a Soxhlet-based procedure or a supercritical fluid extraction method with nitrous oxide in the dynamic mode. The authors claim to have been able to achieve quantitative recovery of PCDDs by SFE in 2 hours. We were unable to reproduce their results due to analytical interferences attributed to impurities in the nitrous oxide used as the supercritical fluid in our experiments.

In this paper, we report our experimental results for quantifying PCDDs in fly ash samples, treated with formic acid or HCl prior to the supercritical fluid extraction. A comparison between dynamic leaching and static modes of extraction is also discussed.

EXPERIMENTAL

Fly Ash Samples

Grab samples of fly ash were collected by the Ontario Ministry of the Environment and were provided to us by Dr. Thompson. Samples were stored in a closed container at room temperature and protected from light.

Sample Extraction and Concentration

A 10g sample of fly ash was treated with 3 percent hydrochloric acid (20 mL) for 1 hour. Afterwards, it was filtered under suction using a pre-washed fiberglass filter (Whatman GF/A), washed with 50 mL distilled water and air dried. Samples were spiked with chlorinated C-13 labelled PCDDs as internal standard (2,6). The aliquot (2 g) was extracted overnight (approx. 20 hrs) with 200 mL toluene in a medium porosity Soxhlet thimble. The toluene extract was washed with 100 mL of 0.05 M Na_3PO_4, and further concentrated to 1 mL before cleanup on a Florisil column (7). Polychlorinated benzenes and biphenyls were eluted with n-hexane (20 mL) and the PCDDs with n-hexane + diethyl ether (1:1).

Supercritical Fluid Extraction

A supercritical fluid extraction system SFC SUPREX MPS-225 was employed in our studies. The system can use cryogenic trapping which allows the collection of all extracted compounds in a precise temperature controlled manner. After trapping, the cryogenically collected analytes were re-trapped in a suitable solvent or introduced directly onto the GC/MS. In our case, we retrapped the analytes in 5 mL of n-hexane.

Approximately 25 mg of an homogenized aliquot of fly ash, previously treated with formic/or hydrochloric acid (75 μL), was precisely weighed into a 1 mL volume extractor. A schematic diagram of the SFE system is shown in Figure 1. The extraction was performed in the static mode using nitrous oxide (Linde, Union Carbide, Mississauga, Ont.) as previously described (4). The extraction process was pre-programmed using the integrated software to perform the valve switching and to control temperature via the cryogenic trapping system. An example of the timing sequence is given in Table 1. A restrictor having an internal diameter of 25 mm and 20 cm in length was used and changed after every third extraction.

Table 1. An Example of the Extraction Sequence Program
Supercritical Fluid : Nitrous Oxide + 5 % Toluene
Temperature : 45°C

Stage	Mode	Pressure (atm)	Time (min)	Selection	Injection
Initiate		400	0.0	Pos.1	Load
1	Step	400	2.0	Pos.1	Load
2	Step	400	0.5	Pos.2	Load
3	Step	400	2.0	Pos.1	Load
:	:	:	:	:	:
15	Step	400	0.5	Pos.2	Load
16	Continuous leaching	400	4.0	Pos.2	Load

Quantification of PCDDs

Identification and quantification of PCDDs by means of HRGC/MS was done by spiking the fly ash samples with a labelled PCDD mixture as internal standard. Quantification of the C-13 labelled dioxin mixture was carried out using a reference standard mixture of unlabelled and labelled dioxins consisting of one isomer for each congener group. The twenty ions monitored during the analysis are identified in Table 2.

Table 2. Selected ions employed for quantification of chlorinated dioxins.

Chlorinated dioxin	m/z (1)	m/z (2)	Ret. window (min)
4CDD unlabelled	319.9	321.9	14 - 18
4CDD labelled	331.9	333.9	14 - 18
5CDD unlabelled	353.9	355.9	18 - 21
5CDD labelled	365.9	367.9	18 - 21
6CDD unlabelled	387.9	389.9	21 - 24
6CDD labelled	399.9	401.9	21 - 24
7CDD unlabelled	421.8	423.8	24 - 27
7CDD labelled	433.8	435.8	24 - 27
8CDD unlabelled	457.7	459.7	27 - 31
8CDD labelled	469.7	471.7	27 - 31

A mixture of C-13 labelled dioxins consisting of 2,3,7,8-4CDD, 1,2,3,7,8-5CDD, 1,2,3,4,7,8-6CDD, 1,2,3,4,6,7,8-7CDD and octachloro dibenzo-p-dioxin (8CDD) in toluene was used.

The HRGC-MS system employed an Hewlett-Packard Model HP5880 gas chromatograph fitted with a 30 m x 0.25 mm i.d SE-52 crosslinked column and a mass selective detector (HP 5970). The following GC operating conditions were employed to separate dioxin congeners: injection temperature 250°C, interface temperature 250°C, initial time 3.0 min, programmed at 20°C/min to 180°C then at 5°C/min to 270°C, final time 20 minutes. Two microliter injections were made in the splitless mode using toluene as solvent and a purge time of 0.5 minutes. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The end of the open tubular column was inserted directly into the ion source of the mass selective detector operated at 70 eV in the electron impact (EI) mode. The electron multiplier was set at 2200 Volts and the dwell time at 200 ms per peak.

Screening of a sample for the presence of dioxins was performed in the selected ion monitoring (SIM) using predetermined time windows (Table 2). These chromatographic windows were determined by running a mixture of all available dioxin congeners and by monitoring simultaneously the most intense ion for each congener group. The detection of the three specified ions in the correct ratios and at the right retention times provided confirmation of the presence of a particular dioxin isomer and the sample was then subjected to the quantitation procedure.

The quantification protocol described here is similar to that reported by Norstrom et al (8). It involves quantification by monitoring for the correct congener group through its specified time window, using the most intense ion in the molecular cluster of the unlabelled and C-13 labelled (internal standard) dioxins. Use is made of the quantification and reporting software provided with the HP 5970 data acquisition system. The quantification is based on the responses of the C-13 internal standards. This automatically corrects for losses of material during the cleanup and for variations in chromatographic conditions between injections. A mixture consisting of equal concentrations of unlabelled and C-13 labelled dioxins is first run in order to calibrate the system. Recoveries are determined against an external standard.

Method Optimization

Various sets of experimental conditions have been investigated in order to optimize the method. Selected variables are summarized in Table 3. Additional variables for SFE, such as pressure, temperature and time have been published previously (4).

RESULTS AND DISCUSSION

Analytical supercritical fluid extraction is primarily concerned with the recovery of a complex mixture of solutes and not the selective extraction of a single analyte. Thus SFE conditions must be optimized for selected groups of analytes and the determination of these conditions can be very time consuming. The extraction of an analyte depends on competition between adsorption to the matrix and solubilization by the supercritical fluid. The importance of the competition between adsorption and desorption processes during supercritical fluid extraction has not received sufficient attention in the development of this analytical extraction technique.

The fly ash matrix may contain up to 30 percent of carbon. It has been reported (9) that the amount of carbon in the fly ash affects the efficiency of dioxins recovery. To evaluate the effect of surface area and porosity, we selected three kinds of carbon samples having surface areas of 12, 100 and >1000 m^2/g, respectively. Each carbon sample was spiked with known amount of C-13 labelled PCDD mixture. The SFE was carried out with N2O+ methanol (2%) without pretreatment, at 400 atm and 45°C under conditions referenced as of program A in the footnote of Table 3. Our SFE results indicate that approximately 23 percent recovery of PCDDs was obtained with the graphitized carbon black samples, characterized by the smallest surface area. Carbon black samples characterized by greater surface area adsorbed PCDDs even more strongly. Recovery from the 100 m^2/g carbon was only 4 percent and carbon with more than 1000 m^2/g showed less than 1% recovery of PCDDs. Graphitized carbon with smaller surface area exhibits only dispersive interactions between its surface and the pi-electrons of the aromatic ring of the substrate structure. Carbon black is an adsorbent characterized by a large surface area and can adsorb very strongly analytes with structures containing pi-electrons. Quantitative removal of these analytes from the surface is very difficult.

Our previous study (4) indicated that a mixture of nitrous oxide + methanol (2%) can be used successfully to extract 2,3,7,8-TCDD from sediments.

The static mode for extracting PCDDs was preferred since the total amount of nitrous oxide used for extraction is less than 30 percent of that used in continuous leaching. Smaller amounts of impurities introduced with the extraction fluid may be tolerated during quantification.

With no certified standard of PCDDs for the fly ash samples currently available, all extraction data were compared with those obtained with the Soxhlet extraction technique. Two types of municipal fly ash samples were employed for both the Soxhlet and the SF extraction experiments. Triplicate runs were carried out on each sample and a mixture of C-13 labelled PCDD was used as a spike. The results of the analyses are presented in Table 4.

Table 4 shows the results of Soxhlet extraction analyses of PCDDs in the above-mentioned municipal incinerator fly ash samples. Toluene was employed as an extraction solvent, since it gives the highest extraction recovery of PCDDs from fly ash matrices (2). Both fly ash samples were treated with HCl prior to extraction. The results indicate a large standard deviation in triplicate analyses. It is unknown, whether this inconsistency is caused by an uneven distribution of PCDDs in the matrix or from an incomplete extraction of homogenized samples.

Experimental conditions for the supercritical fluid extraction of PCDDs from two different fly ash matrices are summarized in Table 3. All experiments in this study, with the exceptions of experiment No. 8 and 11 were performed using the lower PCDD concentration level fly ash sample. The remaining two experiments employed the higher PCDD level fly ash sample.

There are nine variables considered important for optimization but two of them, the sample size and extraction temperature were kept constant during the entire study. The results obtained are provided in Table 5. Percent recovery data at two levels are illustrated in Figures 2 and 3. The reported yields represent corrected recoveries of PCDDs as calculated on the basis of C-13 labelled PCDD spikes.

In experiment 1, a continuous leaching with N_2O + methanol (2%) was

applied for 60 minutes to a sample not spiked with any C-13 labelled PCDD. The data shows that recovery of PCDDs averages 15 to 20% as compared to Soxhlet extraction and represents true recovery values. Experiment no. 2 duplicated the SFE conditions described in our previous study (4). This extraction was carried out with CO2 and the fly ash sample was treated in the extractor with 50 mL of formic acid and allowed to equilibrate for 30 minutes prior to extraction. Recoveries under the specified conditions indicate low extractability of native PCDDs and C-13 labelled PCDDs in the fly ash (64 %), when compared to the results obtained via Soxhlet extraction of the same sample. Nevertheless, the results indicate that pretreatment of the fly ash matrix with acid improves significantly the recovery of PCDDs.

The results of experiment no.3 corresponding to a continuous leaching of PCDDs by nitrous oxide containing 5 % toluene at 400 atm and 45°C, after pretreatment of the matrix with formic acid (50 mL), provided 110.5% recovery of PCDDs. Some of the advantages of the static mode of extraction over the leaching mode can be observed in Figure 2. The homolog composition indicates that tetrachlorinated congeners are partially stripped from the trapping solution. This can be expected, considering that the solvent is purged with the expanded gas at 240 mL/min. Octachloro dibenzo-p-dioxin is also SF-extracted with a lower yield in experiment no.3 for the same reason. The major homolog groups from 5CDD to 7CDD show similar composition patterns in Table 5.

The effect of the duration of the extraction on the recovery of PCDDs extraction has been evaluated in experiments no. 4 and 5. Results from experiment no.4 carried out at 350 atm with nitrous oxide + methanol (2%) as an entrainer indicate over 121% recovery of PCDDs. In this case, no pretreatment of the fly ash sample with acid was employed to overcome a possible matrix effect. However, the extraction time totalled 150 minutes. With static SF-extraction (experiment 5) using CO2 + toluene (5%) the results indicate that at 400 atm and 45°C and with pretreatment of the fly ash with 50 mL of formic acid, 100% recovery of PCDDs can be achieved in 80 minutes. The recoveries of PCDDs using N2O + toluene (5%) in experiments 6 and 7 confirmed that nitrous oxide is indeed to be preferred as a supercritical fluid for the extraction of dioxins. Doubling the total extraction time in experiment 6 to the total to 80

minutes vs. 40 minutes in experiment no. 7 resulted in only 11.1% increase in yields of PCDDs.

Our results show that employing lower pressures between 300 to 350 atm and shorter extraction times (40 to 60 min) as it was used in experiments no. 9, 10, 12 and 13 resulted in uncomplete recoveries of PCDDs.

Recoveries of PCDDs in exp. 12 and 13 illustrate that using N2O + methanol (2%) at 350 atm, not all congeners are quantitatively extracted. In exp. 12, a selective removal of hydrocarbons and polycyclic aromatic hydrocarbons was achieved using a pre-extraction with ethylene at 200 atm and 20°C during 60 minutes. An almost identical recovery of PCDD was obtained without such pre-extraction as shown by the results of experiments 12 and 13.

It may be concluded that the addition of formic acid or HCl (experiments 6 and 8) to the sample significantly affects extraction yield. This observation is in agreement with previous findings by Scheidl et al (3) who treated fly ash samples with HCl before Soxhlet extraction.

Ranking the results obtained at the lower PCDD concentration level confirmed that the extraction with nitrous oxide + toluene (5%) at 400 atm and 45°C, after pretreatment with formic acid, provides recoveries of PCDDs that match or exceed those of Soxhlet extraction. The static mode of SF-extraction is a better choice because it requires a smaller amount of nitrous oxide and thus, background interference from impurities is significantly lower. An optimum total time for the extraction should be 120 minutes. When for some reason a lower pressure (350 atm) must be used, extraction time must be extended to 150 minutes under the same conditions as above. Thus the time for an extraction must always be considered as a principal variable in SFE experiments.

The results of the experiments performed with higher level PCDD fly ash samples support the conclusions based on those obtained with low level PCDD samples. It is evident that N2O + methanol (2%) at 400 atm and 45°C after pretreatment of the fly ash matrix with formic/hydrochloric acid, provides the best recovery for PCDDs. Experiment 8 confirmed that acidic pre-treatment

followed by SFE with N20 + methanol provided 137% recovery for PCDDs. Given the highest recoveries for internal standard spikes, the results suggested that additional matrix effects were also present. An important difference between experiment no. 8 and 11 worth noting is that the sample in experiment 8 was meshed (60-80 mesh sieve), while sample in experiment 11 was not sieved. This variable was not investigated in depth but it is recommended to sieve samples before SFE to assure uniformity of particles in the extractor.

Table 3. Summary of SFE Experimental Conditions
Sample size : 25 mg; Temperature 45°C

Variable	Experiment Number													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Pressure,atm	350	400	400	350	400	400	400	400	350	350	300	350	350	400
No. Replic.	2	1	2	2	1	2	1	3	2	2	3	2	2	2
Sup.Fluid	N_2O	CO_2	NO_2	N_2O	CO_2	N_2O	N_2O	N_2O	CO_2	N_2O	N_2O	N_2O	N_2O	N_2O
Modifier	M	-	T	M	T	T	T	M	M	M	M	M	M	M
Pretreatment	-	F	F	-	F	F	F	HCl	T	T	T	E	-	-
Time-static	-	64	-	120	64	64	32	64	40	40	60	50	40	64
leaching	60	16	60	30	16	16	8	16	10	10	12	16	10	16
Program No.	B	A	B	C	A	A	A	A	C	C	C	D	A	A

Footnote : M - methanol(2%); T - toluene (5%); F - formic acid;
E - preextraction with ethylene; HCl hydrochloric acid.
Program A : 15 steps-static extraction (16 min.)+ 4 minutes leaching usually repeated 2 to 4 times respectively.
Program B : dynamic leaching.
Program C : 20 steps-static; 20 minutes equilibration time + 5 minutes purging, usually repeated 2 to 6 times.
Program D : 12 steps-static, 15 minutes equilibration time + 3 minutes purging.

Table 4. Results from Soxhlet Extraction of Fly Ash Samples Spiked at Two Levels and Corrected for Recovery as Based on C-13 Spikes

Dioxin Sample	4CDD	5CDD	6CDD	7CDD	8CDD	Total
	micrograms/kilogram					
Low level	142	324	548	568	457	2039±216
High level	567	539	1030	903	527	3555±479

Mean values of triplicate analyses

Table 5. Yields of PCDDs from Fly Ash Samples (μg/kg)

Exp.	4CDD	5CDD	6CDD	7CDD	8CDD	Total
			Yield (μg/kg)			
1	12	44	72	124	128	350±42
2	53	167	313	421	320	1274±106
3	122	256	359	795	610	2142±172
4	171	481	572	620	636	2480±134
5	122	324	433	660	521	2060±168
6	144	386	422	614	688	2254±150
7	178	233	495	686	435	2027±166
8	570	900	1120	1090	1210	4890±174
9	81	163	128	202	189	763±49
10	60	191	315	437	517	1520±112
11	520	1070	1650	730	250	4220±488
12	124	190	390	479	420	1603±102
13	127	181	406	515	400	1629±165
14	119	127	567	391	362	1566±171
15	379	607	861	860	571	3278±212

In general, it may be concluded that under the conditions studied SFE was more efficient than the Soxhlet extraction technique, provided that a correction based on the recovery of a C-13 PCDD spike was made. Advantages of the SFE vs. Soxhlet can be measured in saving time required up to 24 hrs to remove PCDDs from a fly ash matrix and another 15 hours for the cleanup and quantification. This time-span can be shortened to 2.5 hours per sample using SFE. However, there is a disadvantage at the moment in that the cost for commercial extractors is relatively high. An operator can handle only one sample at a time using one instrument. If the process is to be automated this drawback would have to be thoroughly evaluated. It is difficult to quantify

improvements in the operator's safety but there is no doubt that handling small quantities of a sample taken for analysis and replacement of large amounts of solvents in the laboratory makes this methodology an attractive analytical technique.

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